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Engineering Science and Technology, an International Journal

journal homepage: www.elsevier.com/locate/jestech

Full Length Article

Effect of bath agitation on surface properties and corrosion behaviour of ENi-P coatings along with annealing temperature



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ARTICLE INFO

Article history:

Received 2 August 2016

Revised 9 September 2016

Accepted 22 September 2016

Available online 29 September 2016

Keywords:

Agitation

ENi-P

Annealing

Corrosion

Microhardness

ABSTRACT

Electroless Nickel-Phosphorus (ENi-P) coating has been considered to be one of the better surface engineering techniques for numerous mechanical, chemical, electrical and electronics applications. However, the achievement of desired coating standards and improved properties of the as-deposited substrate largely depends upon rigid process control measures adopted during the coating process. Towards this, the coating bath chemistry, operating parameters, preparation of surface, and the equipment being used are a few critical variables that have influence on coating deposition rate, uniformity, smoothness and brightness. Endeavour of the present study is to analyze the effect of bath agitation on the properties of ENi-P coatings, with and without heat treatment, carried out on mild steel (MS) as the base material or substrate. Results revealed that a heavy agitation and annealing at 400 °C resulted in 118% increase in microhardness values as against non coated sample without heat treatment. A sharp reduction corrosion rate was observed in the deposit obtained from bath A with nil agitation, as against non-deposited sample. Hence, bath agitation and annealing temperature are pivotal in governing the properties of deposits, thereby enabling manufacturing of substrates and surfaces for specific application and also preventing regular or early failures, with improving service life.

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1. Introduction

Mild steel (MS), also referred to as low carbon steel, is used in a variety of applications involving aviation, automobile, chemical industries, etc. for manufacturing pipes, motorcycle and door frames, automobile chassis, armor, chains, bullets, nuts and bolts, hinges, magnets, cables, wire, knives, gears, pins. However, due to the poor resistance of MS towards corrosion, use of MS in corrosive environments should be avoided, unless some protective deposition is done on its surface. Electroless Nickel-Phosphorus (ENi-P) deposition technique, however, is one such technique that widely influences and enhances the properties of MS, including improvement in corrosion resistance, thereby broadening its applications even in corrosive environment. This is attributed to the formation of a pore-free protective barrier on the surface of the substrate, thereby preventing it from corrosion attack. Any improvement in properties of MS would therefore not only enhance the service life of numerous components, but also result

in increased resistance to failure. ENi-P coatings with high percentage of phosphorous content offer maximum corrosion resistance as against medium or low phosphorous deposits, which offer improved wear resistance [1,2]. The deposit, apart from having high levels of uniformity, has a sharp influence on other properties and attributes like microhardness and surface roughness [3–9]. As machining of any surface results in varying amounts of micro irregularities, this property is referred to as surface roughness. Depending on the application, high or low surface roughness may be desirable. High surface roughness enables trapping of lubricants or paints and prevents undesirable welding or corrosion of parts. Bath agitation plays a crucial role in controlling the particle incorporation into the coating, and hence affecting the surface roughness of the as-deposited samples [10].

On the basis of extensive literature survey undertaken, it is revealed that not much study has been undertaken on ENi-P deposition with bath agitation and heat treatment. In bath agitation of varying levels like mild and heavy, result in the provisioning of fresh bath solution to all parts of the base metal or substrate on which the deposition is being undertaken. In addition, bath agitation result in removal of hydrogen gas that is generated during the deposition process [2]. This not only results in better particle distribution in the solution, but also prevents localized overheating

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Peer review under responsibility of Karabuk University.

of the substrate surface. Heat treatment or annealing process involves heating of the as-deposited substrate to temperatures in the range of 200–500 °C in a muffle furnace. This heating results in change in the crystallinity of the structure and double strengthening of the nickel phosphide (Ni_3P) phase of the coating, thus increasing the microhardness values of the as-deposited samples [11,12].

The present experiment investigates the result of bath agitation, using a magnetic stirrer, on ENi-P coating using mild steel as base substrate. The deposited samples are thereafter subjected to heat treatment/annealing process within the selected range of 200–400 °C and studied for improvement in various properties and characteristics like Surface Morphology, Crystallographic Structure, Microhardness and Surface Roughness (R_a), thereby highlighting the process for manufacturing materials and preparing surfaces with improved properties, and also it gives the higher levels of resistance to failure, which attributes for critical applications in marine, aviation, engineering, automobile, and in various fields. The investigation involves preparation of a suitable chemical bath, maintained at three different levels of bath agitation, which are, nil, mild and heavy, along with heat treatment of the as-deposited samples at 200 °C and 400 °C. Vojtech et al. [13] studied the majority of the heat treatments undertaken on as-deposited samples in the range of 200–500 °C. In this range, coatings subjected to heat treatment at 400 °C reveals most optimum microhardness which viewed highest Ni_3P formation. The microhardness has however found to decrease as the temperatures have been further increased to 450–500 °C. The decrease in microhardness is attributed to the change in grain structure, wherein the grain size is found to increase and to the Ni_3P precipitate coarsening [14]. In view of the foregoing, the temperature range selected for carrying out heat treatment in the present analysis is maintained between at 200 °C and 400 °C.

2. Experimental design

2.1. Experimental setup and Substrate preparation

A mild steel substrate having dimensions 20 mm × 20 mm × 5 mm and consisting of a pin-hole drilled at the corner (for ease of suspension in the chemical bath) has been used for carrying out ENi-P coating. The substrate was subjected to the surface preparation activities prior to coating procedure. The substrate was mechanically cleaned to ensure removal of physical particles/dust, followed by degreasing in acetone. The substrate was thereafter cleaned in 10% NaOH solution at 60 °C, then which the substrate was dipped in 10 ml of 40 percent by volume HCl for 2 min resulting in etching. This ensured thorough removal of any rust particles from the substrate surface. Finally, the substrate was subjected to activation with 50 g/l of NaH_2PO_2 for 10 min, then the substrate was subjected to deposition in the chemical bath for duration of 60 min. On completion of surface activation (pretreatment process), the specimens were placed in the ENi-P bath solution for coating to take place under varying bath agitation levels. The coating was undertaken in three different baths A, B and C, maintained at nil, mild and heavy agitation levels respectively. Mild agitation corresponds to 150 rpm and heavy agitation corresponds to 350 rpm respectively, generated by the magnetic stirrer. The bath composition and operating conditions of ENi-P deposit on mild steel specimens are; nickel sulphate hexahydrate – 30 g/l, sodium hypophosphite monohydrate – 28 g/l, citric acid monohydrate – 12 g/l, propionic acid – 2.2 ml/l, pH – 8, and temperature – 87 ± 1 °C. The experimental setup is shown in Fig. 1. It consists of a heater and magnetic stirrer (Tarsons, Spinot model MC 01) which maintains the temperature at a precision of ± 1 °C

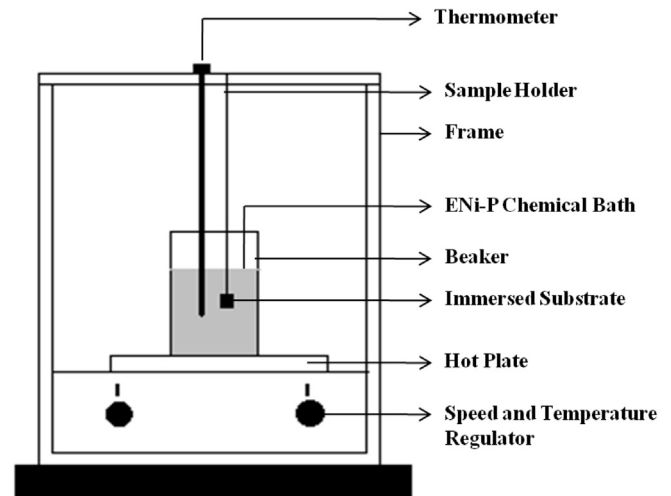


Fig. 1. Experimental setup for ENi-P coating deposition.

and agitation (0–350 rpm). Before and after immersion, the specimens were weighed using an electronic weighing machine. Subsequently, the coating was undertaken by completely dipping the specimens into the electroless solution, for duration of 60 min. On the completion of deposition process, care was taken to ensure thorough cleaning of the coated specimens by rinsing using DI water. The specimens were thereafter dried and safely secured for carrying out the required characterization.

2.2. Analysis of electroless nickel-phosphorus coatings

Field Emission Scanning Electron Microscope (FESEM) [Model: Sigma, Carl Zeiss] was utilized for analyzing the surface morphology of ENi-P coatings prior and post annealing at various temperatures. Energy Dispersive X-ray (EDX) analysis was done in tandem with FESEM to study the chemical composition of the ENi-P coatings in percentage weight (nickel and phosphorus content). XRD [Model Name: Bruker AXS, Germany (D8 Advanced)] was put to use for obtaining the crystallographic structures of the specimens, in which various precipitated phases, both prior and post heat treatments were seen.

2.3. Measurement of micro-hardness and coating rate of ENi-P coatings

Resistance to scratch, indentation or cutting are attributes of material hardness. Microhardness value is a relative measure of the resistance of material subjected to plastic deformation provided by a standard source. The Vickers Hardness (VHN) value can be found from the following well-established formula:

$$VHN = \frac{F(1.854)}{d^2} \quad (1)$$

where, 'F' is load in Newton and 'd' is the mean of two diagonals formed by pyramidal indent in micrometer. A microhardness tester (Wilson Hardness, Model name: Tukon 1202) comprising of a Vickers diamond pyramid indenter was utilized for determining the microhardness of ENi-P coating. The load applied was 500 gm with a dwell time of 10 s with an indentation speed of 50 $\mu\text{m/s}$.

The coating rate of the coating was measured using the under mentioned formula:

$$t = \frac{W_2 - W_1}{\rho * A * T} \quad (2)$$

where, ' t ' is the coating rate ($\mu\text{m/h}$), ' W_1 ' is the weight of substrate before coating (gm), ' W_2 ' is the weight of substrate after coating (gm), ' ρ ' is the density of the deposit (gm/cm^3), ' A ' is the surface area exposed to coating (cm^2), ' T ' is the deposition time in hours.

2.4. Surface roughness and corrosion behaviour of ENi-P coatings

Taylor Hobson surface roughness tester was put to use for calculating and measuring the surface roughness (' R_a ' arithmetic mean of the distances to the median line) values of the ENi-P coated samples. The R_a value was measured as a mean of five values recorded using a stylus instrument, for each substrate. The probe cut-off length was set as 0.8 mm. Gaussian filter and evaluation length, on the other hand, was set at 4 mm with a traverse speed of 1 mm/s, for carrying out the measurement.

The salt spray tests were conducted on chamber makes Advance Equipment with the following chamber parameters: Temperature is $35 \pm 1^\circ\text{C}$, Pressure is 1.7 kg/cm^2 , Solution is 0.5% NaCl solution and time is 240 h.

3. Results and discussion

3.1. Surface morphology and chemical compositions analysis of ENi-P coatings

The surface morphology of ENi-P alloy coating was studied using FESEM. A comparative study of the morphology of the coat-

ings obtained from baths A, B, and C, having nil, mild and heavy agitations respectively is reflected in Fig. 2. It is clear from Fig. 2 (a) that coating obtained from the bath with nil agitation results in distinct cauliflower like nodular structure along with visible grain boundaries and uniform distribution of phosphorus, thereby resulting in good corrosion resistance [15]. This aspect is favourable for various marine applications, wherein the components are subjected to or prone to high levels of corrosion. In the coatings obtained from baths with mild and heavy agitation (Fig. 2b and c), lower phosphorus content with relatively non-uniform distribution of phosphorus was observed, thereby leading to micro cracks or porosity on the coating surface, which may act as breeding ground for corrosion.

In general, it is the phosphorous content present in ENi-P coatings that primarily governs the properties and structure of the resultant coating. Therefore, in order to analyze and appreciate the effect of varying bath agitation on the resultant properties and chemical composition of coatings, EDX analysis has been carried out. On carrying out the analysis, the chemical content of phosphorus in as-deposited ENi-P coatings is as shown in Fig. 2. A sharp variation in phosphorus content was observed in the coatings obtained from baths A, B and C, maintained at nil, mild and heavy agitation respectively. The wt.% of phosphorous in the as-deposited ENi-P coatings obtained from baths A, B and C are 13.5, 5.58 and 4.84 respectively. This clearly indicates that bath agitation plays a crucial role in controlling the incorporation of phosphorus in ENi-P coating.

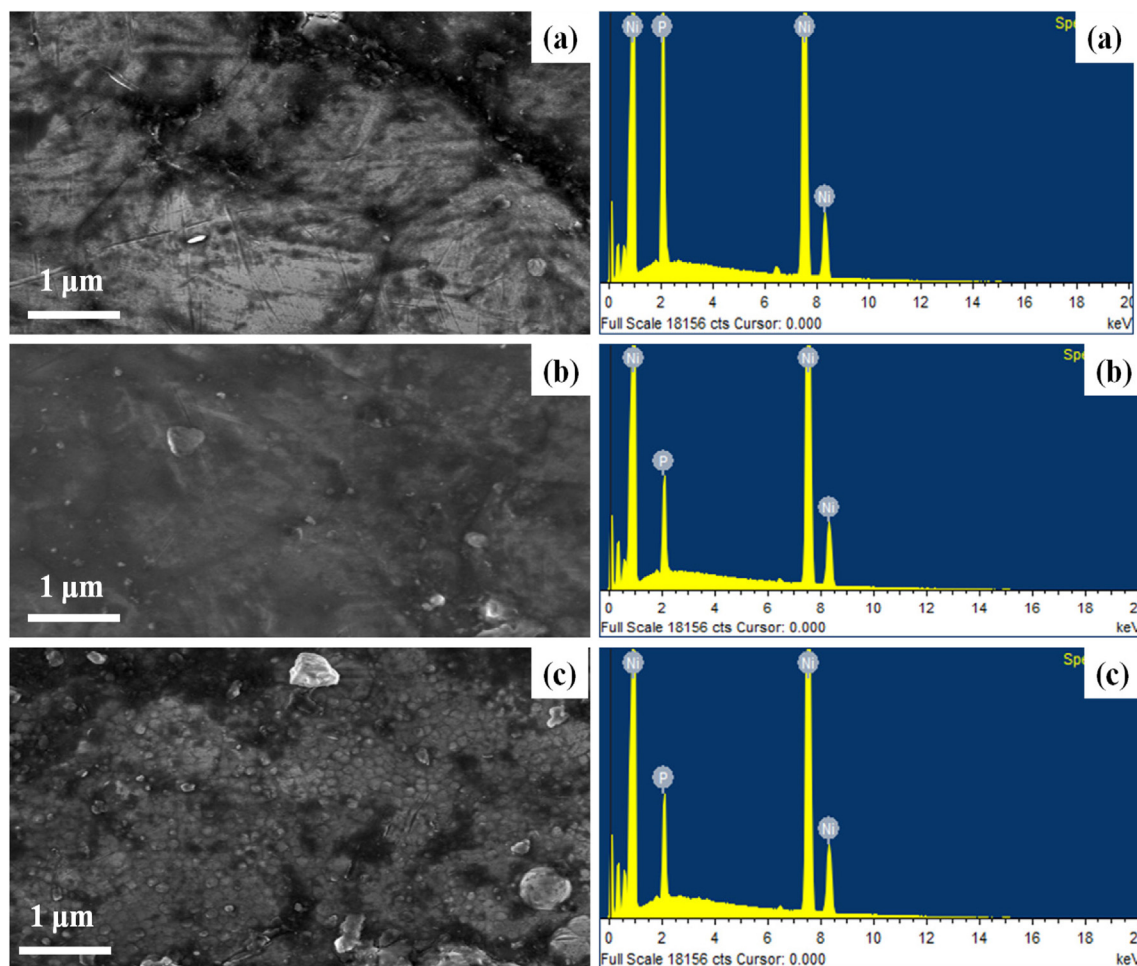


Fig. 2. FESEM morphologies as-plated condition under high magnification at 10.00 KX and EDX analysis of ENi-P deposits (a) bath A, (b) bath B and (c) bath C.

3.2. Coating rate of ENi-P coatings

Literature survey reveals that bath agitation results in removal of hydrogen gas produced during the ENi-P deposition process. This removal of hydrogen gas, thus results in improved levels of coating rate onto the base substrate. Experimental investigation results, as shown in Table 2, reveal that maximum coating rate of 13.9 $\mu\text{m}/\text{h}$ is observed in the coating obtained from Bath C, followed by 13.1 $\mu\text{m}/\text{h}$ and 6.93 $\mu\text{m}/\text{h}$, obtained from baths B and A respectively. This thus indicates that heavy agitation in bath C results in maximum hydrogen gas removal from the bath, followed

Table 2

Chemical composition, coating rate and surface roughness of as-plated condition ENi-P deposits obtained from bath A, B and C.

Level of agitations	Coating rate ($\mu\text{m}/\text{h}$)	Phosphorus content (wt.%)	Surface roughness, R_a (μm)
Bath A	6.93	13.5	0.60
Bath B	13.1	5.58	0.67
Bath C	13.9	4.84	0.83

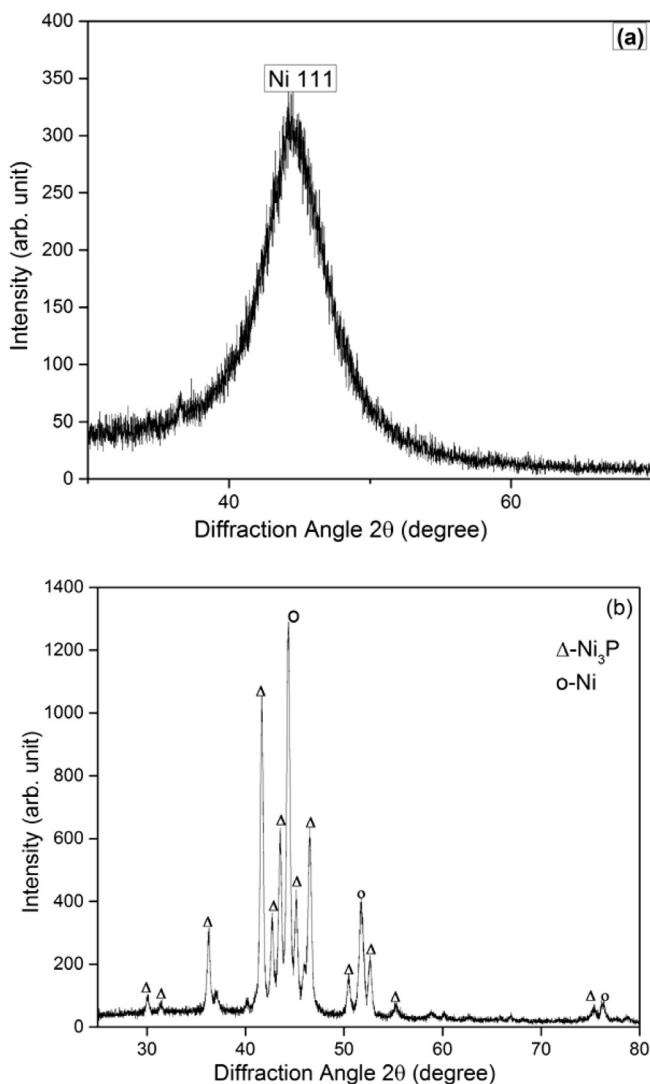


Fig. 3. X-ray diffraction pattern of ENi-P deposits obtained from bath A (a) as-plated and (b) heat-treated at 400 °C for 1 h conditions.

by removal from baths B and A respectively, and hence, affecting the coating rate of ENi-P coatings.

3.3. X-ray diffraction Analysis of ENi-P coatings

In XRD analysis of the obtained coatings from three baths, prior to heat treatment, a single broad peak approaching Ni at $2\theta = 44.8^\circ$ along with numerous diffused peaks were observed. This thereby reflects the presence of a mixture of amorphous and micro-crystalline phase in the plate, view medium phosphorus content in the coating and as a result of the incorporation of phosphorus in nickel matrix [16], thereby exhibiting a plane (1 1 1) of a FCC or face-centered cubic phase of nickel. The same is evident from the diffractogram Figs. 3–5 below. Mai et al. studied that the ENi-P coatings with higher phosphorus content (greater than 7% by wt.) are amorphous in nature [17]. A scrutiny of the diffractogram reveals remarkably high peaks for the coating obtained from agitated baths. However, the absence of well-defined peaks in the coating from the bath agitation is indicative of the amorphous nature of the coating. Post-annealing at 400 °C for one hour, the crystalline structure of Ni_3P phase was observed in coatings obtained from all three baths. Figures also show the enhanced intensity of Ni as well as other peaks of nickel based compounds which appear as a result of annealing process at 400 °C. This is indicative of the fact that on heat treatment, crystallization of the nickel base occurs, thereby resulting in formation of a new Ni_3P phase, which involves diffusion of phosphorous atoms.

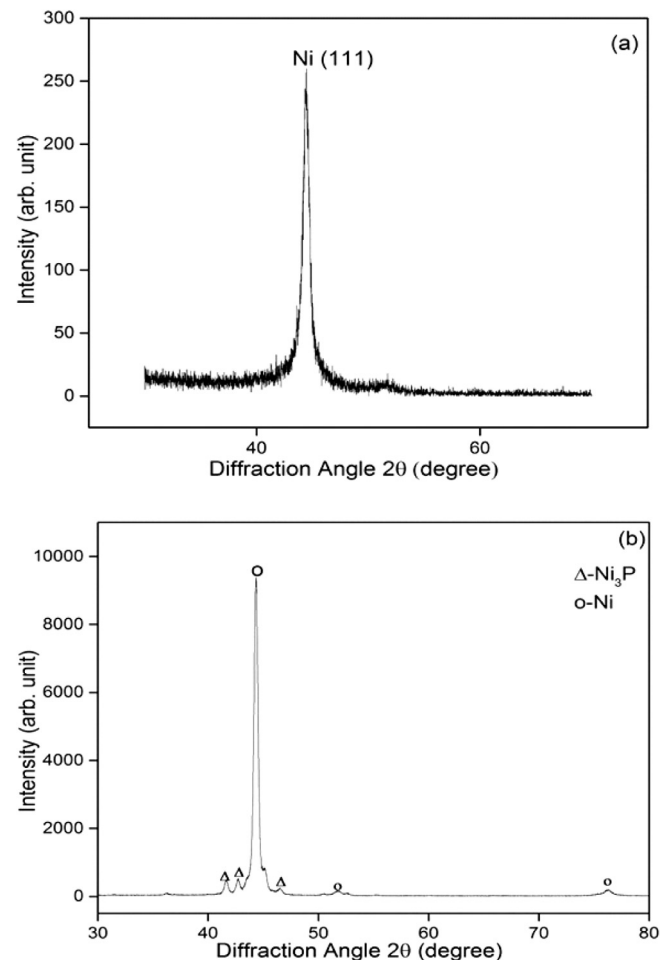


Fig. 4. X-ray diffraction pattern of ENi-P deposits obtained from bath B (a) as-plated and (b) heat-treated at 400 °C for 1 h conditions.

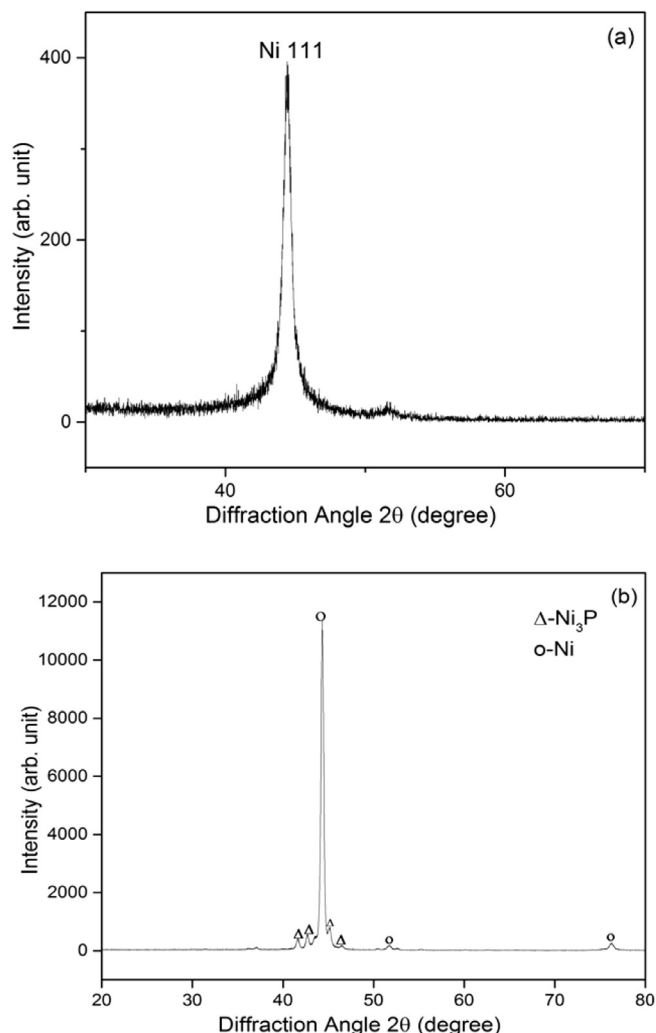


Fig. 5. X-ray diffraction pattern of ENi-P deposits obtained from bath C (a) as-plated and (b) heat-treated at 400 °C for 1 h conditions.

3.4. Effect of heat-treatment on micro-hardness of ENi-P coatings

The report in the literature reveals that the microhardness values exhibited by ENi-P coatings are notably higher than the microhardness values of the conventional electroplated nickel. As depicted in Table 1, the microhardness levels of ENi-P coatings are observed to increase as the bath agitation increases from nil agitation to heavy agitation. Hence, the microhardness value of as-deposited ENi-P coating obtained from bath C is maximum at 405 HV, as against a minimum microhardness value of 305 HV obtained in bath A (nil agitation). It may be noted that the microhardness value of non deposited mild steel sample is 220 HV. The

Table 1
Microhardness of as-plated and heat-treated conditions of ENi-P deposit obtained from bath A, B and C.

Level of agitations	Microhardness* (VHN ₅₀₀)		
	As-plated	Heat-treated	
		200 °C	400 °C
Bath A	305	350	362
Bath B	344	387	408
Bath C	405	443	480

* Average of five determinations.

microhardness values are observed to further increase as the as-deposited samples are subjected to heat treatment or annealing process [18]. It may be noted from Table 1 that the microhardness values of coatings subjected to annealing temperature of 400 °C are much greater than the microhardness values of the as-deposited samples subjected to annealing temperature of 200 °C. The maximum microhardness value obtained is 480 HV, resulting from coating obtained from bath C, when subjected to annealing temperature of 400 °C. This value is 118% greater than the microhardness value of the non deposited mild steel sample. Increase in microhardness view annealing process is attributable to the formation of Ni₃P phase, which happens to be a hard compound [19]. This strengthening effect not only improves the microhardness values of the deposits, but also improves the resistance to failure or results in higher service life of components, thereby preventing early or frequent failures. Any further increase in annealing temperature would result in decrease in microhardness values view coarsening of Ni₃P phase [14].

3.5. Surface roughness of ENi-P coatings

The average surface roughness of MS substrate prior to deposition was measured to be 1.21 μm. Table 2 results show that the R_a value decreases as the mild steel samples were subjected to ENi-P deposition. However, bath agitation was crucial in determining the R_a values, as the as-deposited substrate from bath C possessed greater surface roughness of 0.83 μm, as against the as-deposited substrate obtained from bath A, having minimum R_a value of 0.60 μm with nil agitation, which is attributed to the centrifugal effect caused due to agitation [20] resulting in higher surface roughness at greater agitation levels.

3.6. Corrosion rate analysis of electroless ENi-P deposit

The as-deposited specimens obtained from baths A, B and C was exposed to salt spray in the Salt Water Spray Chamber. This was followed degreasing the specimens in acetone, then the specimens were thoroughly rinsed in DI water before corrosion testing. The time taken for appearance of rust on the as-deposited surface was carefully recorded so as to assess the rate of corrosion of each specimen. The rate of corrosion was calculated utilising the weight loss method and is expressed as millimeter per year (mmpy). The mathematical equation for calculating the corrosion rate (C.R.) is given as [21]:

$$C.R. (\times 10^{-3} \text{ mmpy}) = \frac{87.6 * W}{\rho * A * T}$$

where, W is the weight loss (mg), ρ is density of specimen (g/cm³), A is the area of specimen (cm²) and T is the exposure time in hours. Fig. 6 depicts the corrosion rate with respect to bath agitation of the as-deposited specimens obtained from Salt Water Spray Chamber respectively. The corrosion rate thus obtained for as-deposited of ENi-P deposits from baths A, B and C reveals that the specimen from bath A has the least corrosion rate or maximum corrosion resistance, followed by the specimen from bath B and bath C respectively. The values of corrosion rate obtained for as-deposited ENi-P deposited specimens from baths C, B and A on being subjected to salt spray for 240 h are, and 4.5 mmpy, 4.1 mmpy and 1.6 mmpy respectively. This is clearly indicative of the fact that appropriate control of the bath agitation can lead to a sharp reduction in the corrosion rate of the as-deposited specimens, as it is the agitation that controls the amount of phosphorous in deposit, thus controlling the corrosion levels [15], thereby enhancing the material or substrate property and improving service life in humid/marine environment and for underground pipeline laying applications.

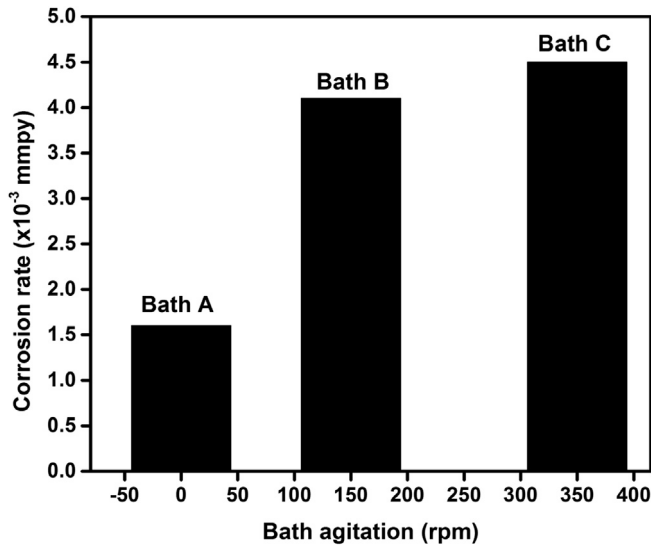


Fig. 6. Effect of bath agitation as-deposited condition of ENi-P deposits on the corrosion rate.

4. Conclusions

Some of the experimental investigations based on the specific coating conditions to focus the influence of bath agitation and annealing temperature during ENi-P coating have been investigated with respect to coating characteristic/properties. It has been observed that the agitation plays an important role in maintaining uniform heat distribution and thorough mixing of the solution, thereby providing a good lustrous appearance and improved service life of the substrate surface. Following addition critical conclusions are drawn from the investigations:-

- Bath agitation and annealing process in a specific temperature range is instrumental in determining the characteristics and properties of the deposits.
- The XRD plots showed that the ENi-P coatings are amorphous in as-deposited condition. However, post annealing process at 400 °C for an hour, the coatings turns out to be crystalline with different nickel phosphide (Ni_3P) compounds and the crystalline nature of these deposits suggests its aptness for use in high wear resistance applications.
- A reduction in the corrosion rate has been noticed as the bath agitation decreases from heavy agitation to nil agitation which is primarily due to the higher phosphorus content at bath A (nil agitation).
- The micro hardness of the coating increases with increase in annealing temperature from 200 °C to 400 °C, for an investigation time period of one hour. It was observed that a maximum hardness of 470 (VHN_{500}) was achieved with heavy agitation at annealing temperature of 400 °C, followed by 408 (VHN_{500}) for mild agitation. The rise in micro-hardness due to the formation of Ni_3P hard compound phase.

- The surface roughness (R_a , μm) of the end product can be regulated by controlling the flow pattern around the substrate. High levels of surface roughness, having values of 0.83 μm were observed for heavy agitation as against relatively lower values of surface roughness, 0.60 μm and 0.67 μm , achieved for nil and mild agitation respectively.

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